PHASE TRANSITION OF PRASEODYMIUM MONO-PNICTIDES UNDER HIGH PRESSURE

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The Phase transition and elastic properties of Praseodymium-monopnictides have been investigated under pressure by means of a modified charge-transfer potential model which incorporates the Coulomb screening due to the delocalization of f-electron of rare-earth atom leading to many-body interactions, along with Coulomb interaction, covalency effect and overlap repulsion extended up to second-nearest neighbours. These compounds undergo transition from NaCl structure to high pressure body-centered tetragonal (BCT) structure (distorted CsCl-type P4/mmm). The calculated values of cohesive energy, lattice constant, phase transition pressure, relative volume collapse. Present model explains the Cauchy's discrepancy correctly.

Keywords: Rare-earth compounds; High pressure phase transition; Equation of state.

1. Introduction

There is a growing experimental and theoretical interest in the study of rare earth (RE) mono-pnictides of praseodymium (PrX : X = P, As, Sb, Bi) due to their intricate electronic structures and other diversified and unusual properties[1,2]. The interest in these materials has further increased after it was demonstrated that they can be grown epitaxially on III-IV semiconductors [3]. These monopnictides crystallize in NaCl crystal structure and can be studied within interaction potential theory which is relatively cheap and easy. From the theoretical point of view, the electronic properties of the RE compounds are mainly determined by the degree of localization of the 4f electrons, the treatment of which presents a considerable challenge to band theory. The PrX Compounds behave similarly to La- and Ce- compounds. X-ray diffraction on PrX (X=P, As and Sb) the NaCl has been performed at high pressures at room temperature [4,5]. The high-pressure phase of PrX is tetragonal (distorted CsCl-type P4/mmm). The powder X-ray diffraction using the synchrotron radiation of cerium and praseodymium monopnictides [CeX and PrX (X=P, As, Sb and Bi)] up to 42 GPa at room temperature has been carried by Svane, *et al.*[7] They have also computed the electronic structures by self-interaction corrected local-spin density approximation. The high pressure

structural behavior of the actinides and pnictides has also been reported by Benedict, *et al.* [8,9]. The pressure induced structural phase transition occurs from B1 phase to body-centered tetragonal structure, which may be viewed as a distorted B2 phase [10]. The isomorphous transformation in PrP occurs at around 26 GPa with a volume collapse of 12.1% [10]. While in PrAs, PrSb and PrBi it occurs at with transition pressures of 27, 13 and 14 GPa [11-13] respectively. Varshney *et al.* the models used by them are basic for explaining the crystal properties but they exclude Coulomb screening effect due to many-body interactions in the expressions, which play an important role in defining the crystal properties of heavy-earth compounds (HECs) and in particular, their expressions of elastic moduli are not correct. Their expressions actually lead one to $C_{12}=C_{44}$ while their results have shown $C_{12}\neq C_{44}$ which is contradictory and hence their approach is not realistic qualitatively and quantitatively and the results unreliable. To study the high pressure behaviour of these compounds, we have developed an improved potential model which incorporates proper crystal interactions *viz.*, long-range (LR) Coulomb and Coulomb screening due to the delocalization of electron of the rare-earth atom (charge-transfer or many-body interaction (CTI or MBI) [14]) modified by covalency effect [15] and short-range (SR) repulsion extended up to second-nearest neighbours. The expressions derived from the present model are capable of explaining the crystal properties correctly. Therefore, we have used the modified expressions of the second-order elastic constants (SOECs), their combinations, Cauchy's discrepancy, third-order elastic constants (TOECs) and first- and second-order pressure derivatives of SOECs for present study as reported earlier [17-19]. The corrected part has been underlined in these expressions. In this next section, we have described in detail the potential model and followed by methodology used to compute the model parameters. The results have been discussed in section 4.

2. Potential Model

The relative stability of the two competitive phases, *i.e.*, B1 and B2 has been studied by minimizing the Gibbs free (GF) energy ($G=U+PV-TS$) at zero and high pressures using iterative self-consistent method. At phase transition pressure (P_T) both the phases coexist. The cohesive energy is expressed as

$$U(r) = U_{\text{Coul}} + U_{\text{CTI}} + U_{\text{Cov}} + U_{\text{HF}}$$

$$\text{Or } U(r) = -\frac{\alpha_M e^2 Z_m^2}{r} + b \sum_{ij} \beta_{ij} \exp\left(\frac{r_i + r_j - r_{ij}}{\rho}\right) \quad \text{with } Z_m^2 = Z(Z+2nf_m(r))$$

The various terms in above equation have their usual meaning and are well described elsewhere [16]. The value of CTI parameter depends on the nearest neighbour (nn) distance and can be estimated from the analytic expression $f_{\text{CTI}}(r) = f_0 e^{-r/\rho}$ with f_0 as CTI parameter, here ρ , is range parameter. The values of the model parameters, *viz.* b , ρ and $f_m(r)$ have been obtained from the equilibrium condition and compressibility or bulk modulus (B_T) as $dU/dr|_{r=r_0}$ and $d^2U/dr^2=9KrB_T$ with $K(=V/r^3)$ as structure constant.

The potential has been used to derive the expressions of the elastic moduli, their combinations and pressure derivatives on the lines suggested by [14]. Here, it is interesting to note that the corrected term as underlined in these expressions [16] were ignored by Gour, *et al.* [17] and Varshney, *et al.* [18] which upon further examination actually lead one to $C_{12}=C_{44}$ while our analysis naturally expresses the Cauchy's discrepancy ($C_{12}-C_{44} \neq 0$) in terms of CTI parameter. The relation for Cauchy's discrepancy from the present derivations comes out to be $C_{12}-C_{44} = 9.3204Z e^2 a^f(r)/4a^4$ for NaCl structure.

The expressions for TOECs, first- and second-order pressure derivatives of SOECs have also been derived on the lines given by [14]. The higher derivatives of the CTI parameter $f(r)$, *i.e.*, $a^f(r)$, $a^2f''(r)$ and $a^3f'''(r)$ have been evaluated from the analytical expression $f(r) = f_0 e^{-r/\rho}$. The method of determination of the parameters has been described in the following section.

3. Computation of Model Parameters

The MCTP model has low parametric nature and hence consists of only three parameters, namely, hardness (b), range (ρ) and modified CTI parameter $f_m(r)$. The values of these model parameters have been calculated from the self-consistent method using the compressibility or bulk modulus and equilibrium condition [16] and experimental values of lattice constant to obtain the optimized values of cohesive energy and volume which in term gives the values of model parameters. The values of the input data along with the computed model parameters are listed in Table 1.

4. Results and Discussions

In order to check the relative stability of the two competitive phases, we have minimized the lattice energies in both real B1 ($G_{B1}(r_{B1}) = U_{B1}(r_{B1}) + PV_{B1}-TS$) and high pressure phase B2 ($G_{B2}(r_{B2}) = U_{B2}(r_{B2}) + PV_{B2}-TS$) phases at ambient conditions by self-consistent technique to obtain the consistent value of lattice constant at ambient and high pressure conditions. To check the relative stability, we have minimized the lattice energies in both B1 and B2 phases at ambient conditions corresponding to equilibrium

Table 1: Input data r_0 (in $10^{-10}m$), B_T (in GPa) and model parameters b (in $10^{-19}J$), ρ (in $10^{-10}m$) and f_0 (unit free) for Pr-monopnictides.

Solids	Input data		Model parameters		
	r_0	B_T	b	ρ	f_0
PrP	2.950 ^a	74±2 ^a	156.88	0.321	958.17
PrAs	3.000 ^a	100±7 ^a	148.21	0.312	1455.00
PrSb	3.175 ^b	44±5 ^a	215.55	0.338	1603.99
PrBi	3.230 ^a	40±5 ^a	180.87	0.368	810.14

^aRef. [1]; ^b Ref. [4]

interionic separations $r_{B1}(r_{B2})$ using the MCTP model parameters listed in Table 1. The corresponding Gibbs free (GF) energies $G_{B1}(r_{B1})$ and $G_{B2}(r_{B2})$ at difference pressures have also been computed and plotted in figure 1. The pressure at which these GF energies cut each other have been marked by arrows as the phase transition pressure (P_T) in these figures and the values of P_T have also been reported in Table 2 along with experimental and other theoretical values. The GF energy difference $\Delta G [= G_{B2}(r_{B2}) - G_{B1}(r_{B1})]$ has also been computed as a function of pressure. It is seen that the value of ΔG at zero pressure is positive in all the cases which is the requirement for correct stability of the competitive phases.

Fig. 1 Variation of Gibbs free energy in B1 and B2 phase with pressure for Pr-monopnictides.

Fig. 2 Variation of reduced volume ($V(P)/V(0)$) with pressure for Pr-monopnictides.

Thus the present model predicts correctly that all the Pr-monopnictides are thermodynamically and mechanically stable in B1 phase at ambient conditions. The value of G_{B1} remains minimum up to just before P_T and becomes equal to G_{B2} at P_T exhibiting the coexistence of both the phases at this pressure. Beyond this pressure the energy in B2 phase becomes more negative as compared to that in B1 phase predicting thereby that the high pressure B2 phase is now thermodynamically and mechanically stable as compared to B1 phase. It may be seen from this table that the values of P_T computed by us are in good agreement with experimental data [13] and better than those obtained by earlier theoretical workers [19,20].

These self-consistent values of lattice constant have been used to compute the reduced volume ($V(P)/V(0)$) at different pressure in both B1 and B2 phases. The values of reduced volume at different pressures in both the phases have been plotted in figure 2 to obtain the equation of state (EOS) and in consequence the % volume collapse ($V(P_T)/V(0)$) at P_T for these compounds. These values along with P_T have also been reported in Table 2. Our computed values of P_T ($\approx 25.5, 26.7, 12.9$ and 13.6 GPa) and % volume collapse ($\approx 9.3, 9.3, 11.4$ and 9.6) are in good agreement with the experimental data [13] and better than those obtained by earlier workers [19,20] for PrP, PrAs, PrSb and PrBi, respectively.

Table 2: Calculated values of interionic separation (r_{B1} and r_{B2} in 10^{-10} m), Gibbs free energy (G_{B1}) and its difference ΔG (in kJ/mol), phase transition pressure (P_T in GPa) and % volume collapse ($V(P_T)/V(0)$) for Pr-monopnictides.

Solids	r_{B1}	r_{B2}	G_{B1}	ΔG	P_T	$\% \Delta V(P_T)/V(0)$	References
PrP	2.94	3.13	-2177.3	63.1	25.5	9.3	Present
	2.95	-	-	-	26	-	Expt. [13]
	-	-	-	-	25	8.1	Others [19]
	-	-	-	-	16	12.1	Others [20]
PrAs	2.98	3.19	-2207.1	64.6	26.7	9.3	Present
	3.00	-	-	-	27	9.0	Expt. [13]
	3.01	3.18	-2788.5	93.3	26	8.6	Others [19]
	-	-	-	-	12	-	Others [20]
PrSb	3.21	3.32	-2023.7	47.7	12.9	11.4	Present
	3.19	-	-	-	13	11.0	Expt. [13]
	3.20	3.37	-1882.8	60.6	13	9.7	Others [19]
	-	-	-	-	8	8.9	Others [20]
PrBi	3.26	3.40	-2011.2	50.3	13.6	9.6	Present
	3.23	-	-	-	14	8.0	Expt. [13]
	3.24	3.42	-1816.2	61.2	13.4	9.0	Others [19]
	-	-	-	-	-	8.7	Others [20]

4.1. Elastic properties

To analyses the mechanical strength of these compounds, we have computed SOECs and their combinations, Cauchy’s discrepancy and Poisson’s ratio (σ) at ambient condition as well as at high pressures.

Acknowledgment

The authors are thankful to and UGC and DST, New Delhi for financial support.

References

1. F. Hullinger, in Hand Book on the Physics and Chemistry of Rare Earths, vol. 4, K.A. Gschneidner Jr and L. Eyring, eds., North Holland Physics Publishing, New York, 1979.

2. G. Pagare, V. Srivastava, S.P. Sanyal, and R.K. Singh, Phys. Stat. Sol. (b) 241 (2004), 3197.

3. Allen S J, Brehmer D and Palmstrom C J Rare Earth Doped Semiconductors vol 301, ed G S Pomrenka, P B Klein and D W Langer (Pittsburg, PA: Materials Research Society) 1993.

4. J.M. Leger, K. Oki, J. Rossat-Mignod, J. Phys. C 17 (1984) 4935.

5. J.M. Leger, K. Oki, J. Rossat-Mignod, O. Vogt, J. Phys. 46 (1985) 889.

6. A. Svane, Z. Szotek, W.M. Temmerman, and H. Winter, Solid State Commun. 102 (1997) 477.

7. A. Svane, Z. Szotek, W.M. Temmerman, J. Laegsgaard, and H. Winter, J. Phys.: Condens. Matter 10 (1998), 5325.

8. U. Benedict, S. Dabos-Seignon, J.P. Dancausse, M. Gensini, G. Gering, S. Heathman, H. Luo, J. Staun Olsen, L. Gerward, and R.G. Haire, J. Alloys, Compd. 181 (1992),12.

9. U. Benedict, J. Alloys. Compd. 223 (1995), 225.

10. T. Adachi, I. Shirotnani, J. Hayashi, and O. Shimomura,Phys. Lett. A 250 (1998), 393.

11. I. Shirotnani, K. Yamanashi, J. Hayashi, Y. Tanaka, and N. Ishimatsu, J. Phys.: Condens. Matter 13 (2001), 1946.

12. J. Hayashi, I. Shirotani, Y. Tanaka, T. Adachi, O. Shimomura, and T. Kikegawa, *Solid State Commun.* 114 (2000), 565.
13. I. Shirotani, J. Hayashi, K. Yamanashi, K. Hirano, T. Adachi, N. Ishimatsu, O. Shimomura, and T. Kikegawa, *Physica B* 334 (2003), 174.
14. R.K. Singh, *Phys. Rep.* 85 (1982), 259.
15. K. Motida, *J. Phys. Soc. Japan.* 55 (1986), 1636.
16. D.C. Gupta and K.C. Singh, *Phase transitions* 83 (2010), 182; *J. Alloys Compd.* 499 (2010), 90; *IL Nuovo Cimento D9* (1987), 1253.
17. A. Gour, S. Singh and R.K. Singh, *Central Europ. J. Phys.*, 5 (2007), 576.
18. D. Varshney, N. Kaurav, P. Sharma, S. Shah and R.K. Singh, *Phys. Stat. Sol. (b)* 241 (2004), 3179; *J. Alloys Compd.* 495 (2010) 23. [and references therein].
19. P. Soni, G. Pagare, V. Shrivastava, S.P. Sanyal, *Phase Transition* 82, (2009), 530.
20. G. Vaitheeswaran, L. Petit, A. Svane, V. Kanchana, M. Rajagopalan, *J. Phys.: Condens. Matter* 16 (2004), 4440. R. Loren and D. B. Benson, *J. Comput. System Sci.* 27, 400 (1983).